

Chemistry of Epoxy Compounds. XVIII.¹ Epoxidation of Linolenic (*cis,cis,cis*-9,12,15- Octadecatrienoic) Acid²

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In the peracetic acid epoxidation of a series of natural triglycerides, ranging in iodine number from 64 to 207, it was shown that the ratio of oxirane formation to total oxidation (as measured by disappearance of unsaturation) decreased as the unsaturation of the triglycerides increased.³ The anomalous results were attributed in an undefined way to the polyunsaturated components present in the highly unsaturated triglycerides, but no explicit explanation was offered for this phenomenon.

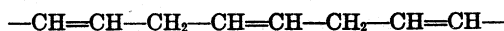
It has been known for a long time that monounsaturated long chain compounds containing isolated double bonds can be more or less quantitatively epoxidized with peracetic acid.^{4,5} Recently, it was shown that linoleic (*cis,cis*-9,12-octadecadienoic) acid, the major diunsaturated component of natural triglycerides, undergoes similar epoxidation.⁶ This note describes a study of the epoxidation of the trienoic acid, linolenic (*cis,cis,cis*-9,12,15-octadecatrienoic) acid, with peracetic and perpelargonic acids, the isolation of 9,12,15-triepoxy stearic acid, and an explanation for the anomalous results mentioned earlier. Although there are references in the older literature to the attempted epoxidation of linolenic acid,^{4,5} highly impure starting materials were employed, the reactions were not followed kinetically, and products were not characterized.

In the reaction of linolenic acid (1 mole) with an excess of peracetic acid in acetic acid solution, calculated consumption of peracid (3 moles) is 90% complete within 1 hr. and 98% complete in 3 to 6 hr. at room temperature or below. In the latter case, the crude reaction product contains only two instead of the anticipated three oxirane groups even though the residual unsaturation may be less than 2% of the original. Thus the ratio of oxirane formation to total oxidation is about 65%. The ester number of the crude reaction product suggests that one oxirane group has been largely converted to ester, probably by a ring opening reaction with acetic acid which is present in large excess. The facile opening of one oxirane ring is unexpected but it accounts for the anomalous results in the peracetic acid epoxidation of highly unsaturated triglycerides.

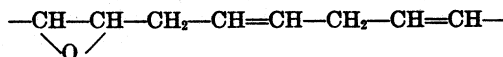
Occasionally, however, 9,12,15-triepoxy stearic acid, m.p. 71°, can be isolated in about 10% yield from the crude reaction product.

Epoxidation of linolenic acid (1 mole) with perpelargonic acid (3 moles) in ether solution is considerably slower than with peracetic acid in acetic acid. More significant, however, is that one can observe a differential rate of epoxidation in this system, whereas in the acetic acid system discussed the over-all high rate masks this difference. Epoxidation of two of the three double bonds in linolenic acid is relatively rapid (5 hr. reaction time) but the third double bond is consumed extremely slowly (40 additional hr.). Although perpelargonic acid is being consumed during the latter period, oxirane does not increase because the rates of ring opening and of epoxidation are essentially identical.

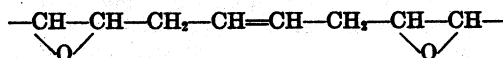
The results of the kinetic study of the epoxidation of linolenic acid with perpelargonic acid in ether can be readily explained. Let us consider the central portion of the linolenic acid molecule:



If one assumes that all three double bonds are equally susceptible to epoxidation, initial attack is twice as likely to occur at one of the outside double bonds of this system as at the central one:



When one outside double bond is epoxidized, the central double bond becomes less susceptible to attack than before because of the electronic influence of the oxirane group.⁷ The other outside double bond should then be preferentially epoxidized but at a rate essentially the same as that of the first outside double bond:



When the central double bond is in close proximity to two oxirane groups, a large drop in reaction rate should be (and is) experienced. At this stage, however, epoxidation and ring opening become competitive and no increase in oxirane content is observed.⁸

When the central double bond is epoxidized first, the rate of epoxidation of both outside double bonds should be reduced to the same extent. This phenomenon is probably unimportant kinetically, since

(7) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947). There are only a few clean-cut cases of the effect of a neighboring oxirane group on the rate of epoxidation of an adjacent double bond. The best known one is the epoxidation of 1,3-butadiene.⁹

(8) After this manuscript had been prepared, the paper by L. Desalbres, B. Lahourcade, and J. Rache [*Bull. Soc. Chim.*, **761**, (1956)], in which the conjugated triene, alloocimene, was epoxidized with peracetic acid, came to our attention. In this case, as with linolenic acid, the reaction was very exothermic and polymer formation occurred, but most important, the outside two double bonds were preferentially epoxidized yielding an isolable diepoxide.

(1) Paper XVII is *Ind. Eng. Chem.*, **47**, 2304 (1955).

(2) Presented at the Spring Meeting of the American Chemical Society, Miami, Fla., April 7-12, 1957.

(3) T. W. Findley, D. Swern, and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).

(4) D. Swern, *Org. Reactions*, **VII**, Chapter 7, (1953).

(5) D. Swern, *Chem. Revs.*, **45**, 1 (1949).

(6) D. Swern and G. B. Dickel, *J. Am. Chem. Soc.*, **76**, 1957 (1954).

initial attack at the central double bond should occur much less frequently than at the outside double bonds. Initial epoxidation of the central double bond, however, will explain the formation of small amounts of 9,12,15-triepoxystearic acid.

The above explanation is also applicable to systems containing more than three double bonds. Interpretation is a little more complicated but the conclusion is the same, namely, that at least one double bond epoxidizes so slowly that ring opening prevents the formation of a fully epoxidized product.

Reaction of linolenic acid with peracetic acid in excess acetic acid under conditions arranged for complete ring opening also proceeds anomalously. The reaction product contains no oxirane oxygen and only two ester groups instead of the anticipated three. The high viscosity of the resulting product suggests that some polymerization has also occurred.

EXPERIMENTAL

Starting materials. Linolenic acid (iodine number 250 and composition: 84% linolenic acid, 14% linoleic acid, 2% saturated acids) was prepared from linseed oil fatty acids by a urea complex separation.⁹ Peracetic acid in acetic acid solution was a commercial product. The preparation of perpelargonic acid in ether solution has already been described.¹⁰

Epoxidation of linolenic acid with peracetic acid. In a 3-neck flask equipped with an efficient stirrer, a thermometer, and a dropping funnel,¹¹ 50 g. (0.49 mole of double bond) of linolenic acid was placed. The flask was immersed in an ice water bath and 175 g. (0.69 mole; 40% excess) of approximately 30% peracetic acid in acetic acid containing 10.5 g. of sodium acetate trihydrate was added dropwise over a 1-hr. period with good agitation. The reaction was vigorously exothermic; the temperature was maintained at 20–25° by adjusting the rate of addition of peracid. Thirty min. after the addition was complete, analysis showed that at least 90% of the calculated quantity of peracid had been consumed

but peracid continued to be consumed for 3 to 6 additional hours. Similar results were obtained at 5–8°. The reaction mixture was poured into several volumes of cold water and the oily layer was dissolved in ether. The ether solution was washed with water until acid free (10 washes), dried, and the ether was evaporated, the last traces under high vacuum. The residue was a pale yellow oil which weighed 49 g.

Anal. Oxirane oxygen, 9.7%¹²; neut. equiv. 360; saponification equiv. 292; iodine number, 2.

Crystallization of the crude reaction product from two volumes of 80:20 acetone:water at –20° yielded 8 g. of white solid, which on recrystallization from the same volume of acetone at –20° yielded 3 g. of 9,12,15-triepoxystearic acid, m.p. 70.0–70.7°.

Anal. Calcd. for $C_{18}H_{30}O_5$: Oxirane oxygen, 14.7%; neut. equiv. 326. Found: Oxirane oxygen, 13.9%; neut. equiv. 322. The isolation of triepoxystearic acid could not always be repeated particularly in cases where the oxirane oxygen content of the crude reaction product was about 8.7, a value much closer to that calculated for a (diepoxy)(hydroxyacet-oxy)stearic acid.

When the epoxidation reaction temperature was allowed to rise to about 60–70° during addition of peracetic acid and then held at 20–25° for 6 hr., the product obtained was a viscous, salvelike mass.

Anal. Oxirane oxygen, 0%; neut. equiv. 450; saponification equiv. 290; iodine number, 6.

Epoxidation of linolenic acid with perpelargonic acid. To a solution of 26 g. (0.15 mole) of perpelargonic acid in 120 ml. of ether, 13.9 g. (0.15 mole of double bond) of linolenic acid was added at 20–25° with stirring. Samples (1 ml.) were withdrawn periodically and peracid content was determined.

Reaction Time, Hr.	Moles of Peracid Consumed per Mole of Linolenic Acid
0	0
1	0.98
2	1.5
3	1.6
5	1.9
21	2.4
28	2.5
44	2.7
51	2.7

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(12) D. Swern, T. W. Findley, G. N. Billen, and J. T. Scanlan, *Anal. Chem.*, 19, 414 (1947).

(13) A laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(9) W. E. Parker and D. Swern, *J. Am. Oil Chemists' Soc.*, 34, 43 (1957).

(10) W. E. Parker, C. Ricciuti, C. L. Ogg, and D. Swern, *J. Am. Chem. Soc.*, 77, 4037 (1955).

(11) The thermometer and dropping funnel were suspended through open necks to avoid pressure build-up if rapid decomposition of peracid occurred.